

## Studies of Stratospheric Bromine Compounds

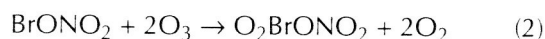
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The current understanding of stratospheric ozone depletion chemistry resulting from halogen compounds indicates that in spite of the fact that the concentration of bromine in the stratosphere is much smaller than that of chlorine, bromine accounts for approximately the same degree of ozone depletion as chlorine because of its much greater ozone-depletion potential. The effectiveness of bromine in promoting ozone loss in the lower stratosphere is related to the fact that most of the bromine resides in more labile forms, relative to chlorine, capable of taking part in the ozone-removal cycles. A greater percentage of bromine is in reactive forms, because the conversion of reactive bromine to the reservoir form hydrogen bromide (HBr) from reactions with methane (CH<sub>4</sub>) or hydrogen (H<sub>2</sub>) is negligible, whereas chlorine atoms can be diverted from the catalytic ozone depletion cycles through the formation of hydrochloric acid (HCl) by reaction with CH<sub>4</sub>, H<sub>2</sub>, or hydrogen dioxide (HO<sub>2</sub>). Further, the destruction rates of HBr and bromine nitrate (BrONO<sub>2</sub>) are much faster than those of the analogous chlorine reservoir species. In response to these findings, there have been a number of experimental and theoretical studies aimed at the detailed characterization of stratospheric bromine compounds over the last several years. It seems natural that BrONO<sub>2</sub> would figure prominently in these studies since the chlorine analog, chlorine nitrate (ClONO<sub>2</sub>), is an important reservoir species. In the lower stratosphere, the formation of BrONO<sub>2</sub> occurs by the termolecular reaction coupling bromine oxide (BrO) and nitrogen dioxide (NO<sub>2</sub>):



(where M is a third body). The destruction of BrONO<sub>2</sub> involves photolysis at ultraviolet wavelengths during the day, leading to a catalytic cycle for ozone destruction. At night, with no photolysis, it has been suggested that BrONO<sub>2</sub> can be removed by heterogeneous reactions. Recently a proposal was made that these heterogeneous reactions of BrONO<sub>2</sub> may also contribute to catalytic destruction of ozone. However, it is proposed here that a more likely explanation for both the elimination of BrONO<sub>2</sub> and the destruction of ozone (O<sub>3</sub>) is provided by an

observation made by researchers in 1974; that is, it was shown that BrONO<sub>2</sub> and O<sub>3</sub> react at 195 kelvin to form a bromide nitrate (O<sub>2</sub>BrONO<sub>2</sub>) molecule (a structure was never determined):



Reaction (2) is likely to be more complicated than the single-step termolecular process presented, probably involving two successive bimolecular processes



Using the tools of computational quantum chemistry, the equilibrium structures, dipole moments, harmonic vibrational frequencies, and infrared intensities of the reactants and products of reactions (3) and (4) have been determined. In order to assess the reliability of these calculations, results for BrONO<sub>2</sub> have been compared with very-high-level singles and doubles coupled cluster theory calculations with a perturbational estimate for triples (denoted as CCSD(T)) and also with experiment where available. Heats of formation of some of these compounds have been evaluated, and the energetics of possible dissociation pathways assessed. We are not aware of any experimental data for the OBrONO<sub>2</sub> and O<sub>2</sub>BrONO<sub>2</sub> compounds. The transition state for reaction (3) has been examined and the barrier height has been determined.

The implications of this work are significant: if this reaction occurs in the stratosphere, particularly during low Sun conditions, then it may greatly enhance the role of bromine in catalyzing ozone destruction in the stratosphere. Also significant is the very real possibility that BrONO<sub>2</sub> may not be a reservoir species for bromine under any stratospheric conditions, a result of its reaction with ozone, contrary to common understanding.

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